What is Nanoscience?

1

1.1 About size scales

Nanoscience is about the phenomena that occur in systems with nanometer dimensions. Some of the unique aspects of nanosystems arise solely from the tiny size of the systems. Nano is about as small as it gets in the world of regular chemistry, materials science, and biology. The diameter of a hydrogen atom is about one-tenth of a nanometer, so the nanometer scale is the very smallest scale on which we might consider building machines on the basis of the principles we learn from everyday mechanics, using the 1000 or so hydrogen atoms we could pack into a cube of size 1 nm × 1 nm × 1 nm. If this is all that there was to nanoscience, it would still be remarkable because of the incredible difference in scale between the nano world and the regular macroscopic world around us. In 1959, Richard Feynman gave a talk to the American Physical Society in which he laid out some of the consequences of measuring and manipulating materials at the nanoscale. This talk, "There is plenty of room at the bottom," is reproduced in its entirety in Appendix B. It does a far better job than ever I could of laying out the consequences of a technology that allows us to carry out routine manipulations of materials at the nanoscale and if you have not already read it, you should interrupt this introduction to read it now.

The remarkable technological implications laid out in Feynman's talk form the basis of most people's impression of Nanoscience. But there is more to Nanoscience than technology. Nanoscience is where atomic physics converges with the physics and chemistry of complex systems. Quantum mechanics dominates the world of the atom, but typical nanosystems may contain from hundreds to tens of thousands of atoms. In nanostructures, we have, layered on top of quantum mechanics, the statistical behavior of a large collection of interacting atoms. From this mixture of quantum behavior and statistical complexity, many phenomena emerge. They span the gamut from nanoscale physics to chemical reactions to biological processes. The value of this rich behavior is enhanced when one realizes that the total number of atoms in the systems is still small enough that many problems in Nanoscience are amenable to modern computational techniques. Thus studies at the nanometer scale have much in common, whether they are carried out in physics, materials science, chemistry, or biology. Just as important as the technological implications, in my view, is the unifying core of scientific ideas at the heart of Nanoscience. This book seeks to build this common core and to demonstrate its application in several disciplines.

In this introductory chapter we will start with technology, that is, those applications that flow from the ability to manipulate materials on the nanometer scale. We will then go on to examine the scientific phenomena that dominate nanoscale systems.

In order to appreciate the technological implications of working at the nanoscale, one must appreciate the incredible scale difference between our regular microscopic world and the atomic world. There are wonderful Web sites that allow the user to zoom in from astronomical scales to subatomic scales by stepping through factors of 10 in size. This exercise is highly recommended, but here we will look at size scales from a chemical perspective.

One mole of any material (e.g., 28 g of silicon) contains Avogadro's number of atoms (i.e., 6.023×10^{23} atoms). This is a fantastic number of atoms. Exponential notation has hardened us to large numbers, so we will look a little further into what numbers as large as this mean.

I like the story of Caesar's last breath: Julius Caesar was murdered on March 15 in 44 B.C. Caesar's lungs, like our lungs, probably exhaled about 1 L of gas with each breath. Since one mole of an ideal gas at standard temperature and pressure occupies 22.4 L, Julius Caesar breathed out about 0.05 mole of N_2 gas as he fell to the ground uttering his famous last words "Et tu Brute?" In the intervening two millennia, these (mostly nitrogen) molecules have had ample time to disperse themselves evenly throughout the atmosphere of the earth. The mass of the Earth's atmosphere is 5×10^{18} kg, of which 80% is N_2 gas which has an atomic weight of 28 g/mole (2×14). There are therefore $0.8 \times 5 \times 10^{18}/0.028 \approx 1.4 \times 10^{20}$ moles of nitrogen gas in the earth's atmosphere, of which 0.05 mole was exhaled by Caesar. So each mole of our atmosphere contains 3.6×10^{-22} moles of Caesar's nitrogen, or about 200 molecules. Thus in each of our breaths, we inhale about 0.05×200 or 10 molecules of Caesar's last breath! The number is probably a little less because of sequestration of nitrogen by plants, but we can see that the enormous size of Avogadro's number draws us to the conclusion that we share each breath with the last lungful exhaled by Caesar. We should remember Caesar as we inhale on the Ides of March. This vast size of Avogadro's number underlies much of the technology discussed by Feynman in his 1959 talk.

1.2 History

Feynman's 1959 talk is often cited as a source of inspiration for Nanoscience, but it was virtually unknown outside of his small audience at the time and only published as a scientific paper in 1992.[1] Nanoscience really sprang into the public consciousness sometime after the invention of the scanning tunneling microscope (STM) in 1981.[2] Here was an amazing tool that could image and manipulate atoms. Atomic scale imaging had been possible in the past with multimillion-dollar transmission electron microscopes, but the STM was a benchtop tool that a graduate student could assemble for a few hundred dollars. The First International Conference on Scanning Tunneling Microscopy was held in Santiago De Compostela, Spain, July 14–18, 1986 (becoming a yearly fixture thereafter with an exponential growth in the number of papers presented). The impact of the STM on surface science was already so great at this time that the 1986 Nobel Prize in physics was awarded to Gerd Binning and Heinrich Rohrer for their invention of the STM. (It was shared with Ernst Ruska, one of the inventors of the electron microscope.) Fueled by the low cost and ease of building atomic resolution microscopes, interest in Nanoscience spread like wildfire, and by the time of the Second International Conference on Scanning Tunneling Microscopy, papers were presented that reported images of biological molecules.[3,4] The invention of the atomic force microscope (AFM) in 1986[5] greatly extended the reach of these tools. Now insulating materials could be imaged with atomic resolution and new types of direct measurement and manipulation on the atomic scale were made possible. The chemists could image directly some of the fantastic structures they had only dreamed of making, and a bright young biochemist in New York, Ned Seeman, was able to realize his dream[6] of building nanoscale machines with self-assembly of DNA molecules. Thus was born the field of DNA nanotechnology.[7] Major government funding of Nanoscience as a separate discipline began in the 1990s, with considerable subsequent impact on inventions in the development of technology.[8] Those of us who were swept up in this field found biologists, engineers, chemists, and materials scientists (and even geologists) knocking on the doors of our physics labs. The days of research within the narrow confines of one traditional discipline were over.

1.3 Feynman scorecard

If you have not already done so, you now have to read Feynman's talk in Appendix B in order to follow this discussion.

How well did Feynman do? A detailed analysis shows a remarkable success rate. I count 10 successes and 5 questionable predictions. A good grounding in physics makes for a better futurist, at least in this area. Here we take each specific prediction in turn and see how it has turned out.

Electron beam lithography: Talking of using electron beams, demagnified in an electron microscope, to write small features: "We can reverse the lens of an electron microscope in order to demagnify as well as magnify . . . This, when you demagnify it 25,000×, it is still 80 Å in diameter – 32 atoms across." Current e-beam technology allows features as small as about 10 nm to be written,[9] close to the prediction. Figure 1.1 shows a tiny Fresnel lens made by

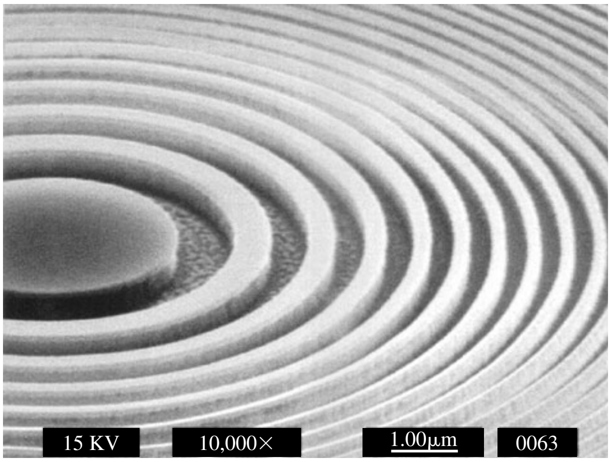

Fig. 1.1 Fresnel lens for focusing X-rays. Submicron features were patterned into a resist using an electron beam (Courtesy of C. David, PSI).

electron beam lithography. It was built to focus X-rays, so the distance between the rings is tens of nanometers. We will discuss this technique in Chapter 5.

Stamping out nanostructures: Feynman predicted that nanostructures could be "printed" directly on to surfaces: "We would just have to press the same metal plate again into the plastic and we would have another copy." George Whitesides has developed a stamping technology based on silicone rubber stamps that are cured on top of silicon nanostructures, leaving an imprint of the nano-features on the surface of the stamp. The stamp can then be used to print out multiple copies of the original (laboriously manufactured) nanostructure very rapidly.[10] Stamp technology is covered in Chapter 5.

Using ions to etch structures: "A source of ions, sent through the lens in reverse, could be focused to a very small spot." Focused ion beams (FIBs) are now used as "nanoscale milling machines," rapidly prototyping nanoscale structures by selectively bombarding away surface atoms with a beam of focused high-energy ions.[11] The FIB is another tool dealt with in Chapter 5.

Three-dimensional high-density storage: "Now, instead of writing everything, as I did before, on the *surface* of the head of a pin, I am going to use the interior of the material as well." Modern integrated circuits have complex three-dimensional structures, built up layer by layer,[12] but high-density information storage in three dimensions has yet to be realized on the nanoscale.

Solving the atomic structure of complex biological molecules by direct imaging: "The wavelength of an electron is only 1/20 of an Å. So it should be possible to see the individual atoms." Electron microscopes can image at the atomic level, but beam damage limits the resolution obtained with biological molecules. Structures have been solved to the nanometer scale by averaging images from large arrays of molecules embedded in ice.[13] Figure 1.2 shows the structure of a complex protein assembly reconstructed from low-dose electron microscopy of a layer of protein frozen in a thin film of ice. Nanoscale microscopy is covered in Chapter 4.

Chemical analysis by imaging atoms: "It would be very easy to make an analysis of any complicated chemical substance; all one would have to do is look at it and see where the atoms are." The very highest resolution electron microscope images have given insight into chemical bonding, but only in very special circumstances.[14] But atomic scale analysis is possible via electron beam induced X-ray emission in dry samples, and the AFM can identify single molecules via specific interactions with molecules tethered to the probe.

Machines the size of biological motors: "Consider the possibility that we too can make a thing very small, which does what we want—that we can manufacture an object that maneuvers at that level! . . . Consider any machine—for example, an automobile—and ask about the problems of making an infinitesimal machine like it." Some tiny nanomotors have been constructed[15,16] but, as we shall see, real biological motors operate on very different principles from the motors humans build. A motor that rotates on a carbon nanotube shaft is shown in Fig. 1.3. Biological motors are touched on in Chapter 10.

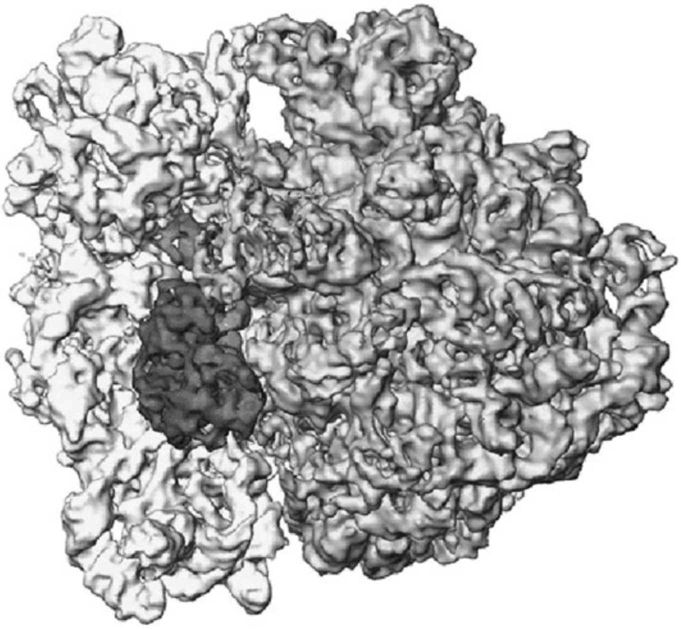

Fig. 1.2 Three-dimensional reconstruction of a protein machine that makes proteins from their RNA code. The complex is about 20 nm in diameter and contains thousands of atoms. This image was obtained by cryoelectron microscopy (LeBarron et al., 2008, made available by Joachim Frank).

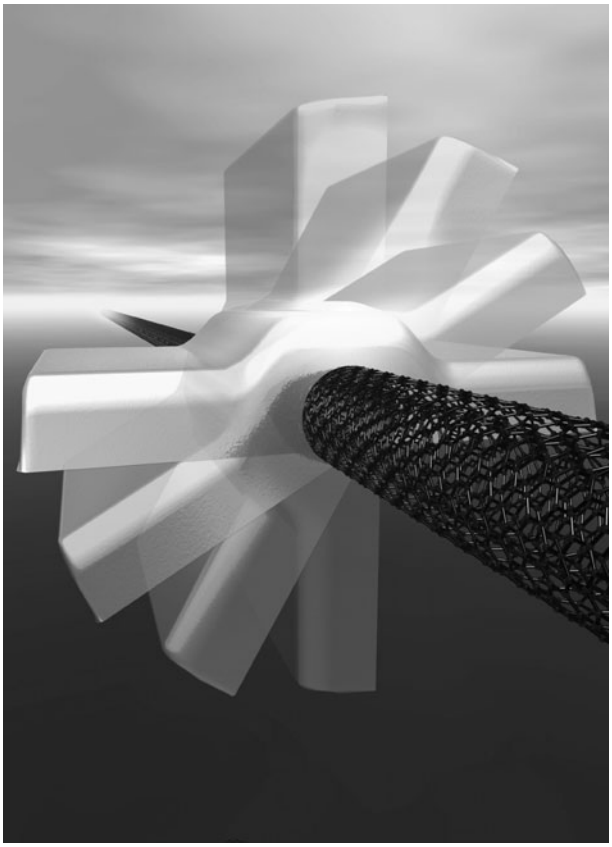

Fig. 1.3 Tiny motor bearing made from a carbon nanotube shaft supported inside a larger nanotube that acts as a bearing (Courtesy of Professor A. Zettl).

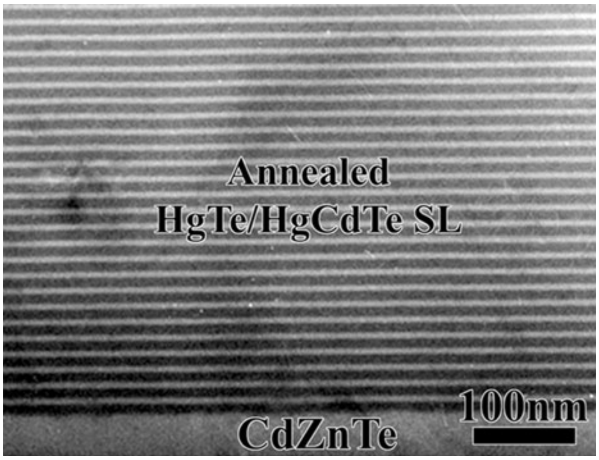

Fig. 1.4 Semiconductor superlattice made from alternating layers of two different compound semiconductors that are each just a few atomic layers thick (Reprinted from The Journal of Crystal Growth, Aoki et al.[18], copyright 2004 with permission from Elsevier).

Miniaturizing computer components to build super computers: "For instance, the wires could be 10 or 100 atoms in diameter . . .. If they had millions of times as many elements, they could make judgments . . . ." These changes have already come about, but as a result of conventional lithography—the smallest features in modern chips are perhaps 1000 atoms across—and computer power has surpassed even this predicted increase. Any one who has struggled with Windows will agree that operating systems have a long way to go before *judgment* is an attribute that springs to mind.

Making atomic scale structures by evaporating layers of atoms: "So, you simply evaporate until you have a block of stuff which has the elements . . . What could we do with layered materials with just the right layers?" Molecular beam epitaxy[17] (MBE) is almost exactly what Feynman had in mind: layers of atoms are formed by projecting hot vapors onto a substrate. Different types of atoms can be projected to form layered structures with nanometer thickness. An example of structure made by layering materials this way is shown in Fig. 1.4. It is a semiconductor "superlattice" made by growing layers of mercury telluride that alternate with layers of mercury cadmium telluride. MBE is discussed in Chapter 5.

Lubricating tiny machines: "But actually we may not have to lubricate at all!" It turns out that many small mechanical structures fail because the closeness of their components leads to parts sticking together through long-range (van der Waals) interatomic forces, and the development of nonstick surfaces for small mechanical components is an important endeavor. But the whole science of lubrication received a boost from the application of AFM methods.[19] Now, at last, we have a probe to study friction where it arises—at the atomic scale at interfaces.

Nanoscale robots that operate inside humans: "It would be interesting if you could swallow the surgeon." Nothing like this has come about, though surgeons do manipulate some remarkable robots remotely. But nanoscale techniques, such as dyes, that report chemical motions in cells (molecular beacons)

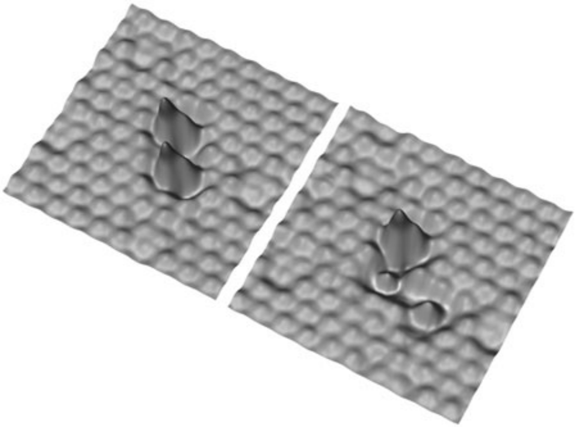

Fig. 1.5 Chemical reaction induced by pushing molecules together with a scanning tunneling microscope (Courtesy of Professor Wilson Ho). See Color Plate 1.

and supramolecular assemblies that carry drugs (e.g., dendrimers) are some of the new technologies emerging from the NIH-sponsored Nanomedicine Initiative.

Exponential manufacturing: machines that make machines and so ad infinitum: "I let each one manufacture 10 copies, so that I would have a hundred hands at the 1/16 size." This idea, of making small machines, that make more even smaller machines that, in turn, make yet more even smaller machines is intriguing, but not realized. However, the idea of exponential growth through copying copies is what lies behind the amazing polymerase chain reaction, the biochemical process that yields macroscopic amounts (micrograms) of identical copies of just one DNA molecule. One molecule is replicated to two, two to four, and so on.

Doing synthesis of complex organic molecules by "pushing atoms together": "We can arrange atoms the way we want." STM has been used to construct some remarkable structures by pushing atoms together (Fig. 1.5),[20] but it is not a very practical way to make new materials because the quantities are so small.

Resonant antennas for light emission and absorption: "It is possible to emit light from a whole set of antennas, like we emit radio waves." This is the modern field known as "nanophotonics." For example, arrays of metal nanoparticles can be used to guide light.[21] Some applications of nanophotonic structures are discussed in Chapter 9.

Using quantum (atomic scale) phenomena in electronic devices: "We could use, not just circuits, but some system involving quantized energy levels, or the interaction of quantized spins." This was a remarkable observation: quantum mechanics offers us completely novel ways to do computations. Electron spin valves have become the dominant readout device in the disk drives.[22] Even more remarkable is the proposal to use the fundamental properties of quantum measurement as a way to do massively parallel computing. The field is called "quantum computing"[23] and it exploits fundamental aspects of quantum measurement (some of which will be introduced when we survey quantum mechanics in the next chapter). Chapter 8 describes the use of molecules as electronic devices and Chapter 7 covers nanoscale solid-state electronic devices.

Feynman started his talk by stating that we should look back from the vantage of the year 2000 and wonder why it took anyone till 1960 to point these things out. I suspect most of us are amazed at just how much Richard Feynman got right in 1959.

1.4 Schrödinger's cat—quantum mechanics in small systems

Atoms are governed by the laws of quantum mechanics, and quantum mechanics is essential for an understanding of atomic physics. The interactions between atoms are governed by quantum mechanics, and so an understanding of quantum mechanics is a prerequisite for understanding the science of chemistry. We will start our study with a survey of quantum mechanics in Chapter 2. It is a conceptually and mathematically challenging topic, to be sure. But modern computational techniques allow for packaged programs that do many of the hard calculations for us. So a conceptual appreciation may be all that is needed to try out some quantum chemical calculations. To that end, I describe the modern technique of *density functional theory* very briefly at the end of Chapter 2. It is the basis of several quantum chemistry packages available over the Web or for downloading on to a laptop computer.

So what has this to do with cats? When many atoms are put together to make a macroscopic object like, for example, a cat, common sense tells us that cats obey the laws of classical physics: when dropped from a tall building they fall according to Newton's laws of motion. I chose the example of the cat as a classical object because of the famous paradox in quantum mechanics known as "Schrödinger's cat." One of the rules of quantum mechanics is that all possible states of a system must be considered in predicting the final state of the system, the final state only emerging on measurement. Quantum mechanics does not specify the result of a measurement, but only the probability a particular final state will be measured. We will examine this rule in detail in the next chapter. "Schrödinger's cat" takes this rule to the point of absurdity. In Schrödinger's thought experiment, a cat is locked in a box together with an instrument for detecting radioactive decay that, once a decay is detected, breaks a vial of poison, killing the cat. In quantum mechanics, the state of the atom is some combination of the decayed and nondecayed state before measurement. Therefore, it could be argued that the quantum description of the entire system of cat, instrument, and radioactive atom is some combination of a live cat and a dead cat. Both exist simultaneously until a measurement is made by opening the box. Quantum mechanics is very subtle here: it is not actually the act of making a measurement that destroys quantum effects. Rather it is an interaction of the quantum system that destroys the quantum effects. And, of course, live cats interact with the outside world very strongly in many ways. Atoms interact with the outside world in many ways as well. Thus, the laws of quantum mechanics predict the way in which atoms form chemical bonds, even though chemical reactions are usually carried out in solutions, where atoms of the solvent are constantly bombarding the atoms as they are undergoing a reaction. The quantum mechanical description works because the energy of this bombardment is much less than the binding energy of electrons to atomic nuclei. Having said that, it turns out that the bombardment plays an important role in chemical reactions in solution. We will discuss the mechanism whereby electron transfer reactions occur in solution in some detail later in Chapter 8. This is, however, an excellent point to turn to the other aspect of physics at the microscopic level that will form a theme of this book: This is the role of fluctuations in complex systems, and particularly in small systems.

1.5 Fluctuations and "Darwinian Nanoscience"

Fluctuations play a large role in small systems simply because they are relatively larger in smaller systems. The total energy contained in the bonds that hold a collection of atoms together decreases with the number of atoms in the system. Importantly, smaller objects have relatively more atoms on their surfaces than in their interior, and these surface atoms are usually more weakly bound than the atoms in the interior. But if the system is in thermal contact with the environment (i.e., in a gas or liquid at room temperature), the average amount of the energy associated with random thermal motion of each atom remains constant (on average) as the system size is decreased at a constant temperature. If the energy of the bonds that hold the system together is comparable to the amount of thermal energy, the system will start to fall apart as a result of random thermal agitation when the total number of bonds becomes small enough. Tables do not fall apart spontaneously, and then reassemble. But proteins fold and unfold, bind with other proteins and randomly unbind. Even small molecules undergoing a chemical reaction that binds them together will spontaneously separate (infrequently if the bond is strong). These fluctuations are what drive the assembly of biological systems and establish the equilibrium between the relative amounts of reactants and products in a system of chemicals undergoing reactions. Such processes are most important in small systems.

But there is more to this story, and this is the part I have called "Darwinian Nanoscience." Darwin's theory of evolution of the species in biology (through selection of the fittest members of a randomized population) is an example of the central role of fluctuations in determining the macroscopic properties of biological systems. This might not seem like a problem of small numbers, but if you are the last dinosaur on the look out for a mate or the virus carrying the first mutant for virulent Spanish Flu, your numbers (and hence the size of the systems) are indeed small. At the end of this book (Chapter 10) we will take a look at how fluctuations drive nanoscale machines such as molecular motors, and how fluctuations in gene expression in small systems (e.g., cells) drive variability in biochemical signaling pathways. We will examine the role of fluctuations in reactions and of solvent fluctuations in mediating electron transfer reactions in solution (Chapter 8). These processes have certain things in common. Fluctuations *dominate* the outcome, and only some special (and rare) set of circumstances lead to the desired end result. The requirement for the processes to be robust is only that the fluctuations sample enough states to make the probability of the rare (but critically important) state very high over some

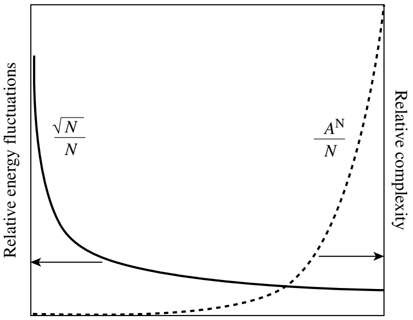

Fig. 1.6 Occurrence of "rare" phenomena as a function of system size. The relative size of energy fluctuations decreases as the square root of the number of particles, while the relative number of arrangements of the system increases approximately exponentially. Here they are plotted as a function of the system size.

period of time. Fluctuations are not just annoying departures from some average properties in these systems. They are the very essence of the process itself. This is illustrated schematically in Fig. 1.6. In Chapter 3, we will use statistical mechanics to derive the result that while the total energy of a system grows with the number of particles, N, in it, *deviations* from this average increase with the square root of the number of particles, $\sqrt{N}$. Thus the fluctuations relative to the mean energy scale as $\sqrt{N}/N$. It is a very general result for many quantities besides the energy of a system. To see this, recall that the standard deviation of the Poisson distribution is given by the square root of its mean,[24] so the fluctuation in repeated counting of N particles is just $\sqrt{N}$. Thus, repeated sampling of the opinions of 100 voters (for example) would return results that varied by 10% most times, purely owing to the random nature of the sampling. $\sqrt{N}/N$ is a function that decreases most rapidly for small values of N (solid curve in Fig. 1.6). For example, an electron transfer reaction requires an energy that is about 50 times the available thermal energy. Such a fluctuation in average energy would require about $(50)^2$ or 2500 particles. Given a fluctuation of the right magnitude of energy to drive some process, what about the probability that it is just the right type of fluctuation? That is to say that the components of the system line up exactly as needed to make some event happen. This will scale with the number of possible arrangements of the system, $N!$, if the particles are all distinct. In general, this complexity is a rapidly increasing function of N, and is shown as an exponential, normalized to the system size also, A^{N}/N (dashed line in Fig. 1.6).

Thus, the probability of the "right" fluctuation occurring increases very rapidly with the number of particles, so that even a modest increase in system size (over the minimum estimated on energy grounds) guarantees a high probability of success. Returning to the example of thermal fluctuations driving an electron transfer reaction, the requirement turns out to be that the molecules surrounding the site of electron transfer spontaneously line up their electric polarizations in the right way. Suppose that the units involved in the electron transfer reaction just discussed were water molecules each occupying about 10^{-2} nm^3, then the volume occupied by 2500 of them is about 25 nm^3 or a cube of sides about 3 nm. The critical size scale where fluctuations are big enough and the system is complex enough is indeed the *nanoscale.*

Biology is complex on a whole series of scales, starting with the nanoscale. A second level of complexity is reached when atoms and molecules are replaced with *genes*, another when atoms and molecules are replaced with *cells*, and yet another when cells are replaced with *whole organisms.*

1.6 Overview of quantum effects and fluctuations in nanostructures

The nanoscientist has no way of escaping the need for some knowledge of both quantum mechanics and statistical mechanics. These disciplines are essential for a conceptual understanding of what makes science so interesting on the nanoscale. On the other hand, there is no way of appreciating the reach of these aspects of physics without a detailed look at how they play out in subjects such as materials science, chemistry, and biology.

Table 1.1 lists many of the phenomena that dominate the nanoscale (and that will be covered in this book) and lists examples of the technologies and other consequences that follow from these phenomena.

Table 1.1 Some phenomena that dominate at the nanoscale and examples of their applications

Phenomenon	Examples
Below a certain length scale (that depends on interaction strengths) behavior must be described using quantum mechanics.	(a) Equilibrium chemistry, at the level of atomic bonding, is described by Schrödinger's equation. The periodic table reflects the allowed symmetries of quantum states in spherical potentials. (b) Quantum "dots" are small semiconductor particles with increased band gaps owing to "size" quantization. (c) Catalysts have novel electronic properties owing both to size and to the relative dominance of surfaces in small particles.
Even materials that interact strongly with the environment can (perhaps at low temperatures) show bulk quantum phenomena if they are small enough.	(a) Small wires and thin films transport electrons in a way that does not obey Ohm's law. This is an example of *mesoscopic* physics. (b) Electrons trapped in thin layers show bulk quantum-like behavior in magnetic fields.
Many processes depend on the number of available energy states per unit energy. This quantity varies with the dimensionality of the system.	Electronic and optical structures that have one (layered), two (wires), or three (dots) very small dimensions exhibit novel properties owing to this modification of the density of states.
Fluctuations are large in small systems. For example, the density of an ideal gas has a mean-square fluctuation given by the number fluctuation in a small volume: $\frac{\langle \Delta N^2 \rangle}{\langle N \rangle^2} = \frac{1}{\langle N \rangle}$.	(a) Fluctuations drive electron transfer reactions and control kinetics. (b) Fluctuations are exploited by enzymes and biological "motors" for function. (c) Fluctuations are important in cells where small numbers of molecules involved in gene expression can lead to large random changes. (d) Fluctuations operate at every level of biology. At the molecular level, random gene splicing generates antibodies and generates protein variations. In populations, they lead to the evolution of species.
Fluctuations in small systems destroy *quantum coherence.* Nano systems may exist at the quantum-classical boundary.	A very difficult and interesting problem: how much of a system is "quantum mechanical" (the chemical bonds in the cellulose that makes up wood) and at what scale is something classical (the table made of wood)? Herein may lie the answer to the Schrödinger's cat paradox.
The effective molarity of reactants that are *confined* in nanostructures may be very high.	(a) Chemical reactions that occur rarely in bulk may be driven by an increased concentration in nano-confinement. (b) Enzymes may *both* concentrate *and* provide the fluctuations that drive electron transfer reactions. (c) Critical spatial assembly of cofactors or *chaperones* may underlie highly specific processes in biology. (d) Diffusion is *geometrically constrained* in the nanostrucures inside a cell.
High information density opens the possibility of pattern analysis of complex many variable processes.	Nanoscale analysis for genomics and proteomics of complex systems like humans?

1.7 What to expect in the rest of this book

Our description of Nanoscience rests on the shoulders of quantum mechanics, statistical mechanics, and chemical kinetics. This essential background forms the materials for Chapters 2 and 3. Our survey is essentially conceptual with mathematics kept to an absolute minimum. I have tried wherever possible to use simple one-dimensional models. Conceptual problems are provided at the end of these chapters in addition to the usual numerical and mathematical problems.

The second part of this book deals with the tools that enable nanotechnology. Chapter 4 is about microscopy and single molecule manipulation. We deal first with scanning probe (atomic force and scanning tunneling) microscopy and then turn to electron microscopy. Finally, we deal with single molecule techniques such as optical tweezers and single molecule fluorescence. These topics give us an understanding of how we characterize nanostructures. The next two chapters deal with different approaches to making nanostructures. In chapter 5, we discuss the traditional "top down" approach to nanofabrication. These methods are extensions of the familiar procedures used in the semiconductor industry to make integrated circuits. Chapter 6 deals with an approach that is more intrinsically "nano," that is, the "bottom up" method based on self-assembly. It is, of course, the path that evolution has taken as replicating living systems have developed on this planet. In this context, the development of techniques that use synthetic DNA to make self-assembling nanostructures is particularly remarkable.

Part three of this book deals with applications. I hope it is more than just a shopping list of nano wizardry. Nanoscience reaches into many disciplines, and thus offers a wonderful basis for an interdisciplinary curriculum. Chapter 7 deals with electrons in nanostructures, and it starts out by presenting a survey of the electronic properties of condensed matter. Chapter 8 introduces the subject of molecular electronics. To do this, this chapter begins with a survey of the electronic properties of molecules from both a theoretical and experimental point of view. The theoretical approach is based on molecular orbital theory. The experimental approach is based on electrochemistry. This is regarded as a complicated topic even by chemistry students, but it is absolutely essential for understanding molecular electronics and Section 8.9 is a self-contained summary of the subject. This chapter is where we treat the Marcus theory of electron transfer, alluded to earlier in this introduction. Marcus theory describes the role of fluctuations in electron transfer, and is an example of what I have called "Darwinian Nanoscience." Chapter 9 is a small and selective survey of nanostructured materials. We have chosen a set of examples where novel material properties follow from restricting the density of states in one or more dimensions. We end with a look at several topics in nanobiology in Chapter 10. There is not room in a book like this for any meaningful survey of modern biology as introductory material in this chapter. But I have attempted to give a bird's eye view of some of what I consider to be some key issues. I hope that this last chapter both interests the reader and motivates a foray into the biological literature.

Fluctuations are a constant theme: We end our chapter on nanobiology with a brief discussion on the role of fluctuations in establishing the random networks that, when acted on by environmental pressures, become the fully formed brains of animals. Darwin's picture of how order emerges from chaos is seen to apply to processes that range from simple chemical reactions to, perhaps, the formation of conscious brains. If this seems a long way from physics, it is worth noting that Frank Wilczek, one of this generation's most talented theoretical physicists, has argued for a "Darwinian" mechanism for the development of the laws of physics that we currently observe.[25,26] Quantum fluctuations at the time of the "big bang" may allow for an infinite variety of universes based on, for example, different values of the electron mass. But only values of the electron mass close to what we observe today are compatible with the universe that supports life as we know it. Wilczek proposes that all possible universes can and do exist; we observe this one precisely because it supports life.

We have strayed a long way from the very small, that is, the subject of Nanoscience. But I hope the reader is convinced that concepts of statistical mechanics and quantum mechanics deserve a place at the center of Nanoscience.

1.8 Bibliography

These are some general texts dealing with nanoscience:

M. Wilson, K. Kannangara, G. Smith, M. Simmons and B. Raguse, Nanotechnology: Basic Science and Emerging Technologies. 2002, Boca Raton, FL: Chapman and Hall/CRC. A comprehensive survey at a fairly elementary level. Though written by a team, the book is well integrated. Chemical structures are emphasized.

M.A. Ratner, D. Ratner and M. Ratner, Nanotechnology: A Gentle Introduction to the Next Big Idea. 2002, Upper Saddle River, NJ: Prentice-Hall. A nontechnical introduction by a famous father and family team.

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G.A. Ozin and A.C. Arsenault, Nanochemistry—A Chemical Approach to Nanomaterials. 2005, Cambridge, UK: RSC Publishing. This book touches on just about every nanostructured material in the current literature. It is a comprehensive catalog.

M. Di Ventra, S. Evoy and J.R. Heflin (eds), Introduction to Nanoscale Science and Technology. 2004, Berlin: Springer. This is a collection of contributions by experts, valuable for plunging into selected topics in greater depth, though little has been done to integrate the material in the book.

1.9 Exercises

Appendix A contains a list of units, conversion factors, physical quantities, and some useful math.

1. *Encyclopedia Britannica on the head of a pin*: Assume that there are 26 volumes (A–Z) each of 1000 pages, each page being 6 × 10 inches. How many times does the entire surface area have to be demagnified to fit into the head of a pin (diameter 0.5 mm)? How does this compare with Feynman's estimate? Assuming 50 characters across a line of each

page, how many iron atoms would there be across each character (Fe atomic diameter = 0.25 nm)?

2. From the ideal gas law ($PV = nRT$) estimate the volume of one mole ($n = 1$) of an ideal gas at standard temperature and pressure (101.3 kPa and a temperature of 273.15 K). Check the assertion about the number of moles in a lungful of air at the start of this chapter.
3. Silicon has a density of 2330 kg^{-3} and an atomic weight of 28.05. Use these data to estimate the volume occupied by a silicon atom.
4. The Pentium IV chip has a die size of 217 mm × 217 mm. How many transistors could be fitted onto the surface of the chip if each could be made from 100 atoms of silicon in a monolayer? Use data from Question 3.
5. What is the size of the current fluctuations (shot noise) in a current of 100 pA over a counting period of one second? Use $e = 1.6 \times 10^{-19}$ C and the expression for number fluctuations in Table 1.1.
6. The electrostatic energy of an electron in the electric field of a nucleus is given by Coulomb's law:

$$E = \frac{1}{4\pi\varepsilon_0}\frac{e^2}{r}.$$

Take $r = 0.1$ nm and estimate this energy. Estimate the kinetic energy of the atom at room temperature (300 K) using $E = \frac{3}{2}k_B T$, where k_B is the Boltzmann's constant (1.38×10^{-23} J/K). Comment on the degree to which electronic structure might be changed by collisions of molecules at room temperature.

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